B7

(19) **State Intellectual Property Office of P.R. China**

(11) **Publication No.** CN 1109022A

(12) **Invention Patent Application Publication Specifications**

(21) Application No.: 94110129.0

(51) **Int. C1**^{6}

C01B 21/06

(43) **Date of Publication:** September 27, 1995

(22) **Date of Application:** 3.21.94

(71) **Applicant:** Dalian Institute of Chemical Physics, Chinese Academy of Sciences

Address: 161 Zhongshan Road
Dalian, Liaoning Province 116012

(72) **Inventors:** Cui [illegible] Liao Shijian Xu Yun

(74) **Patent Agency:** Shenyang Patent Agency of the Chinese Academy of Sciences

Agent: Wang Huimin

No. of Pages of Description:

No. of Pages of Drawings:

(54) **Title of Invention:** Method for synthesis of nanometer size magnesium nitride

(57) **Abstract:**

This invention involves a method for synthesis of nanometer size magnesium nitride, which is made through reaction between high activity magnesium powder and nitrogen under the reaction conditions of normal pressure or a pressure below 5 Mpa and at the temperature of 300 to 600°C. In the process of reaction, it can also be doped with transition metal compounds, such as compounds that contain Ni, Ti or Co elements, to speed up the abovementioned reaction, and the amount of transition metal compound to be doped is 0.1 to 20 mol%. With regard to the method for synthesis of magnesium nitride in this invention, the equipment as needed for reaction is simple, the temperature as required in the reaction conditions is easy to control, the product yield is high, and the produced magnesium nitride is of particle diameter in the range of 3 to 30 nm.

1. This is a preparation method for synthesis of nanometer size magnesium nitride, and it has the following features: high activity magnesium powder is used as reactant magnesium powder, and the synthetic reaction can be performed under the conditions of normal pressure or a pressure below 5 Mpa and at the reaction temperature of 300 to 600°C.
2. With regard to the method for preparation of nanometer size magnesium nitride as mentioned in Claim 1, it has the following features: the reaction can be performed under normal pressure and at the reaction temperature of 300 to 450°C.
3. With regard to the method for preparation of nanometer size magnesium nitride as mentioned in Claim 1, it has the following features: the high activity magnesium powder as the reactant can be in use of the product obtained through heat decomposition under normal pressure or vacuum condition in the process of catalytic synthesis of magnesium hydride or magnesium anthracene.
4. With regard to the method for preparation of nanometer size magnesium nitride as mentioned in Claim 1, it has the following features: in the reaction, it can be doped with transition metal compounds, such as compounds that contain Ni, Ti or Co elements, to considerably speed up the reaction, and the amount of dopant is 0.1 to 20 mol% of the reactant magnesium.

Method for Synthesis of Nanometer Size Magnesium Nitride

This invention involves a method for synthesis of nanometer size magnesium nitride (Mg_sN_2). Specifically, high activity magnesium (Mg) powder is used to react with nitrogen gas under the conditions of normal pressure or increased pressure (0.1 to 5 Mpa) and at the temperature of 300 to 600°C to synthesize nanometer size magnesium nitride.

Mg_sN_2 can be applied in many areas, and it can be used to (1) prepare high rigidity, high heat conduction, corrosion resistant, wear resistant and high temperature resistant nitrides of other elements; (2) prepare special ceramic materials; (3) make foaming agents for special alloys; (4) make special glass; (5) catalyze polymer cross bonding and (6) recover nuclear waste, etc. There are already some patent reports on reactions for synthesis of Mg_sN_2, such as the patent of the former Soviet Union (Year 1961, U.S.S.R. 141, 854) on use of metallic magnesium powder Mg to react above its melting point (648.8°C) with nitrogen gas and to vibrate the reactor in the vertical direction for synthesis of granular Mg_sN_2; the patent of Germany (Year 1958, Ger. 1,034,594) on use of magnesium oxide and coal to react with N_2 under the condition of high temperature for synthesis of Mg_sN_2; and the patent of France (Year 1951, Fr. 996,658) on use of anhydrous magnesium sulfate to react with N_2 at 700°C and in the presence of iron powder for synthesis of Mg_sN_2. In some literature, there are reports that metallic magnesium powder (specific surface area 0.9 m^2/g) can react with N_2 at 450°C under the condition of ionizing radiation, but Mg_sN_2 yield after 18 hours of reaction is only 14% (Fomin, O.K.; et al., *High Energy Chem.*, 1985, 19, 406). The reaction temperature for synthesis of Mg_sN_2 as reported in recent literature is above 600°C. Currently, no report is seen in the literature on the use of high activity magnesium powder Mg for synthesis of Mg_sN_2. No report is seen in the literature either on the synthesis of nanometer size Mg_sN_2.

The purpose of this invention is to provide a method that can be used to synthesize nanometer size magnesium nitride under the conditions of normal pressure or increased pressure (0.1 to 5 Mpa) and at the relatively low temperature of 300 to 600°C.

The following equation can be used to indicate the reaction for synthesis of nanometer size magnesium nitride in this invention:

$$Mg[^{++}] + N_2 \xrightarrow[300 \text{ to } 600°C]{0.1 \text{ to } 5 \text{ Mpa}} Mg_sN_2$$

$Mg[^{++}]$ employs high activity magnesium powder, which can be obtained through the publicly known method for preparation of high activity magnesium powder, and it can also employ the product obtained through heat decomposition under normal

pressure or vacuum conditions in the process of catalytic synthesis of magnesium hydride or magnesium anthracene (*Chemistry Journal*, 1988, 46, 612;). The abovementioned reaction can also be performed under the conditions of normal pressure and at the reaction temperature of 300 to 450°C. In the abovementioned synthetic reaction, the doping of transition metal compounds, such as compounds that contain Ni, Ti or Co elements, can considerably speed up the abovementioned reaction, and the increase of reaction speed varies with different types of dopant. Dopants are doped during the synthesis of MgH_2 or after the synthesis of MgH_2; in the same way, transition metal compounds can be doped during the synthesis of magnesium anthracene or after the synthesis of magnesium anthracene; and the amount of dopant is 0.1 to 20 mol% of the reactant magnesium. When the amount of dopant is less than 0.1%, the doping effect is not obvious; when the amount of dopant is more than 20%, the doping effect is not good either, and there is an excessive amount of impurities and an increase in the cost for synthesis. Implementation cases are presented below to further describe the synthetic method as provided in this invention.

Implementation Case 1 Reaction for synthesis of nanometer size magnesium nitride

Under the protection of inert gas, weigh 0.46 g of high activity magnesium powder Mg and place it in the reaction bulb that is connected to the eudiometer, heat to 450°C with a heat preservation electric heater, and perform the reaction for synthesis of Mg_sN_2 under normal pressure; from the amount of N_2 as absorbed (volume change in the eudiometer), calculate the Mg_sN_2 yield. After 8 hours of reaction, the Mg_sN_2 yield is 69%; after 18 hours of reaction, the Mg_sN_2 yield is 81%. Through measurement by transmission electron microscope, the particle diameter of the product Mg_sN_2 is within the range of 3 to 30 nm.

Implementation Case 2 Synthesis of Mg_sN_2 through doping $Mg[^{++}]$ system

The experiment in Implementation Case 2 is performed in accordance with the experimental conditions and steps as mentioned in Implementation Case 1. Refer to Table 1 for the results.

Table 1 Reaction Results from Synthesis of Mg_sN_2 with Different $Mg[^{++}]$ Systems

Implementation Case	Dopant	Mg_sN_2 Yield (%)					
		Reaction Time (h)					
		1	2	4	6	8	18
1	N/A	37	46	56	65	69	81
2	$NiCl_2$	54	64	73	79	83	92
3	Cp_2TiCl_2*	65	77	86	91	94	99
4	$CoCl_2$	48	56	64	70	76	87

*: Titanocene Dichloride. Reaction conditions: normal pressure (nitrogen gas atmosphere), 450°C. The amount of dopant is 2.5 mol%.

Implementation Case 3 Influence of reaction temperature

The experiment in Implementation Case 3 is performed in accordance with the experimental conditions and steps as mentioned in Implementation Case 1. Refer to Table 2 for the results.

In comparison with Implementation Case 1, Mg_sN_2 is synthesized with commercial magnesium powder

Weigh certain amount of commercial magnesium powder (100 to 200 mesh, and metallic magnesium content is 99%), and perform the reaction for synthesis of Mg_sN_2 in accordance with the experimental conditions and steps as mentioned in Implementation Case 1. After 23 hours of reaction, the Mg_sN_2 yield is 1%.

Based on the abovementioned implementation cases and comparisons, it is obvious that the synthetic method in this invention can be used for quantitative synthesis of nanometer size magnesium nitride (Mg_sN_2) with $Mg[^{++}]$ under the conditions of normal pressure and at the temperature of 450°C. This invention has put forth an important new way to make use of high activity magnesium powder $Mg[^{++}]$. The method in this invention does not have high requirements on reaction equipment, the reaction conditions are under easy control, the raw materials are within easy reach, and the method is simple.

Table 2 Influence of Reaction Temperature on the Reaction for Synthesis of Mg_sN_2

Implementation Case	Reaction Temperature (°C)	Mg_sN_2 Yield (%)					
		Reaction Time (h)					
		1	2	4	6	8	18
2	450	54	.64	73	79	83	92
5	400	20	27	35	42	48	56
6	300	1	2	4	5.5	6.3	10

Reaction conditions: normal pressure (nitrogen gas atmosphere). The dopant is $NiCl_2$, and the amount of dopant is 2.5 mol%.

[12]发明专利申请公开说明书

[21]申请号 94110129.0

[51]Int.Cl[6]
C01B 21/06

[43]公开日 1995年9月27日

[22]申请日 94.3.21
[71]申请人 中国科学院大连化学物理研究所
地址 116012辽宁省大连市中山路161号
[72]发明人 崔 屾 廖世健 徐 筠
[74]专利代理机构 中国科学院沈阳专利事务所
代理人 汪惠民

说明书页数: 附图页数:

[54]发明名称 纳米尺寸氮化镁的合成方法

[57]摘要

一种纳米尺寸氮化镁的合成方法是在常压或5MPa以下的压力下，300～600℃反应条件下，以高活性镁粉与氮反应制得的。该反应过程也可以掺杂过渡金属化合物，如含Ni，Ti，或Co元素的化合物，使上述反应的反应速度加快，过渡金属化合物的掺杂量为0.1～20mol%。本发明合成氮化镁的方法，反应所需设备简单，反应条件温度易于控制，产物收率高，产物氮化镁的颗粒直径范围为3～30nm。

权 利 要 求 书

1. 一种合成纳米尺寸氮化镁的制备方法，其特征在于反应物镁粉采用高活性镁粉，合成反应可在常压或5MPa以下压力下，反应温度在300～600℃的条件下进行。

2. 按照权利要求1所述的纳米尺寸氮化镁的制备方法，其特征在于合成反应可在常压，反应温度300～450℃下进行。

3. 按照权利要求1所述的纳米尺寸氮化镁的制备方法，其特征在于反应物高活性镁粉可以采用催化合成氢化镁或蒽镁在常压或真空条件下热分解所得的产物。

4. 按照权利要求1所述的纳米尺寸氮化镁的制备方法，其特征在于反应中可掺杂过渡金属化合物，如含Ni，Ti，Co元素的化合物，使反应速度显著提高，掺杂物的量为反应物镁的0.1～20mol.%。

纳米尺寸氮化镁的合成方法

本发明涉及一种纳米尺寸氮化镁(Mg_3N_2)的合成方法。具体地说，就是在常压或加压(0.1～5MPa)、300～600℃条件下，使用高活性镁粉Mg与氮气反应，合成纳米尺寸的氮化镁。

Mg_3N_2的应用范围很广，可用于①制备高硬度、高热导、抗腐蚀、抗磨损和耐高温的其它元素的氮化物；②制备特殊的陶瓷材料；③制造特殊合金的发泡剂；④制造特殊玻璃；⑤催化聚合物交连和⑥回收核废料等等。有关合成Mg_3N_2的反应已有一些专利报告，如前苏联专利(1961年，U.S.S.R. 141,854)用金属镁粉Mg在其熔点(648.8℃)以上与氮气反应，并对反应器在垂直方向上施以振动，合成粒状Mg_3N_2；德国专利(1958年，Ger.1,034,594)使用氧化镁和煤，在高温条件下与N_2反应，合成Mg_3N_2；法国专利(1951年，Fr.996,658)使用无水硫酸镁，在700℃、铁粉存在下与N_2反应，合成Mg_3N_2。文献虽曾报道金属镁粉(比表面为0.9m²/g)在电离辐射条件下，可于450℃与N_2反应，但反应18h，Mg_3N_2收率只有14%(Fomin, O.K.; et al., High Energy Chem., 1985, 19, 406)。近期文献中报道的合成Mg_3N_2的反应温度是在600℃以上。目前尚未见用高活性镁粉Mg合成Mg_3N_2的文献报道。也未见合成纳米尺寸Mg_3N_2的文献报道。

本发明的目的是提供一种能在常压或加压(0.1～5MPa)、或较低反应温度300～600℃条件下，合成纳米尺寸的氮化镁的方法。

本发明的合成纳米尺寸氮化镁的反应可用反应式表示为：

$$Mg^{*}+N_2 \xrightarrow[300\sim600℃]{0.1\sim5MPa} Mg_3N_2$$

Mg^{*}是采用高活性镁粉，可按公知制备高活性镁粉的方法获得，也可采

用催化合成氢化镁或蒽镁在常压或真空条件下热分解的产物（化学学报，1988，46，612；）。上述合成反应也可在常压和300～450℃条件下进行。在上述合成反应中，通过掺杂过渡金属化合物，如含Ni，Ti，Co等元素的化合物，可使上述反应的反应速度显著加快，掺杂物种不同，反应速度提高的程度亦不同。掺杂物种是在合成MgH_2时或合成MgH_2后掺入的；同样可在合成蒽镁时或合成蒽镁后掺入过渡金属化合物；掺杂量为反应物镁的0.1～20mol%。当掺杂量小于0.1%时，掺杂效果不明显；掺杂量大于20%时，掺杂效果亦不佳，而且杂质含量过多、合成成本增加。下面通过实例对本发明提供的合成方法作进一步说明。

实例1　合成纳米尺寸氮化镁反应

在惰性气体保护下，称取0.46g高活性镁粉Mg装入与量气筒相连的干燥的反应瓶中，用保温式电炉加热到450℃，在常压下进行合成Mg_3N_2的反应；由吸N_2量（量气筒的体积变化）计算Mg_3N_2的收率。反应8h，Mg_3N_2收率为69%；反应18h，Mg_3N_2收率为81%。利用透射电镜测量，产物Mg_3N_2的颗粒直径范围为3～30nm。

实例2　由掺杂Mg^*体系合成Mg_3N_2

按实例1所述的实验条件及步骤，进行实例2的实验，结果见表1。

表1　由不同Mg^*体系合成Mg_3N_2的反应结果

实例	掺杂物种	Mg_3N_2 收率（%） 反应时间（h） 1	2	4	6	8	18
1	无	37	46	56	65	69	81
2	$NiCl_2$	54	64	73	79	83	92
3	$Cp_2TiCl_2^*$	65	77	86	91	94	99
4	$CoCl_2$	48	56	64	70	76	87

*：二氯二茂钛。反应条件：常压（氮气氛），450℃。掺杂量为2.5mol.%。

实例3 反应温度的影响

按实例1所述的实验条件及步骤，进行实例3的实验，结果见表2。

比较例1 由工业镁粉合成Mg_3N_2

称取一定量的工业镁粉(100～200目，金属镁含量为99%)，按实例1所述的实验条件及步骤，进行合成Mg_3N_2的反应。反应23h，Mg_3N_2收率为1%。

根据上述实例和比较例，可见采用本发明的合成方法，在常压、450℃条件下，由Mg^*能定量合成纳米尺寸的氮化镁(Mg_3N_2)。本发明提出了高活性镁粉Mg^*的一个重要的新用途。本发明的方法对反应设备要求不高，反应条件易控制，原料易得，方法简单。

表2 反应温度对合成Mg_3N_2反应的影响

实例	反应温度 (℃)	Mg_3N_2 收率 (%)					
		反应时间 (h)					
		1	2	4	6	8	18
2	450	54	64	73	79	83	92
5	400	20	27	35	42	48	56
6	300	1	2	4	5.5	6.3	10

反应条件：常压(氮气氛)。掺杂物种为$NiCl_2$，掺杂量为2.5mol.%。

TRANSPERFECT
TRANSLATIONS

THE LEADER IN INTERNATIONAL COMMUNICATIONS

Affidavit of Accuracy

This is to certify the following document: Application No.: 94110129.0, has been translated from Chinese into English by staff members of TransPerfect Translations familiar with both the Chinese and English languages and is to the best of our knowledge, ability and belief, true and accurate translation.

Leigh Wellman

Leigh Wellman
For TransPerfect Translations

Sworn to before me this
Friday, November 17, 2006

Susan Christie

Signature, Notary Public